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(54) CONDUCTIVE POLYMER COMPOSITION AND CONDUCTIVE COMPONENT USING IT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a conductive polymer composition reduced in the dispersion and long-term change of electrical resistance and little in the change with time in environmental conditions, and to provide a conductive component using it.

SOLUTION: The conductive polymer composition comprises an ionically conductive polymer and a lowly moisture-permeable polymer, and is characterized in that the ionically conductive polymer is dynamically vulcanized to constitute the particulate discrete phase; and the lowly moisture-permeable polymer constitutes the continuous phase.

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CLAIMS

[Claim(s)]

[Claim 1] It is the conductive polymer constituent which is a conductive polymer constituent which consists of polymer A which is the macromolecule which has ion conductivity, and polymer B which is a macromolecule with little moisture permeability, and is characterized by having made polymer A into a grain-like discontinuous phase with dynamic vulcanization, and making polymer B a continuous phase. [Claim 2] It is the conductive part which is the conductive polymer constituent which consists of polymer A which is the macromolecule which has ion conductivity, and polymer B which is a macromolecule with little moisture permeability, and is characterized by using a conductive polymer constituent which made polymer A a grain-like discontinuous phase with dynamic vulcanization, and made polymer B a continuous phase.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the suitable conductive polymer constituent for the conductive part of the circumference of photo conductors, such as a copying machine, i.e., an electrification roll, an imprint belt, a transfer roller, etc. especially about a conductive macromolecule constituent.

[0002]

[Description of the Prior Art] While contacting printing paper to a photo conductor in electrophotography equipments, such as a copying machine, a laser beam printer, and regular paper facsimile, and making a toner imprint from the former for example, the imprint belt which conveys printing paper according to electrostatic force is used. If this imprint belt is used, a toner image can be imprinted good, and the printing paper after an imprint can be made to be able to separate from a photo conductor compulsorily, without being comparatively influenced of the class of printing paper, a bearer rate, etc., and it can hold and convey.

[0003] In addition, in order to make the transfer roller and toner which contact the printing paper independently conveyed by it with a conveyance belt on the surface of the photo conductor in which the toner image was formed, and make a toner image imprint on the surface of printing paper stick to a photo conductor, the electrification roll which carries out contact rotation and gives a charge to a photo conductor is known. The imprint belt, the transfer roller, the electrification roll, etc. need to have the conductivity whose volume resistivity is a $10^4 - 10^{12}$ ohm-cm degree. If volume resistivity is less than the above-mentioned range in the case of an imprint belt, the problem on images, such as leak and paper dirt, will occur. When volume resistivity exceeds the above-mentioned range, imprint effectiveness is bad and stops on the other hand, being suitable for practical use. From the electric resistance range of the above [the case of a transfer roller or an electrification roll], if it shifts, a problem will arise similarly.

[0004] Then, conventionally, the conductive belt formed from the conductive rubber constituent which blended with base material rubber the carbon black which is an electronic conductivity grant agent was used as an imprint belt. The same is said of a transfer roller or an electrification roll. However, when an electronic conductivity grant agent was added, and conductivity was adjusted like the above, are put in another way and conductivity is given to rubber only by the electronic conduction by the electronic conductivity grant agent, it is, There was a possibility that the stable image might not be obtained even if the problem of electric resistance varying greatly according to a slight change of the loadings of the electronic conductivity grant agent concerned and the distributed condition of an electronic conductivity grant agent, or conductivity becoming unstable with time arises and it prints as a transfer roller or an electrification roll by using the conductive belt of this configuration as an imprint belt using the conductive roll of this configuration.

[0005] Moreover, when the addition of an electronic conductivity grant agent increased, the dependency to the applied voltage of electric resistance became large, and the problem that a precise applied-voltage control unit is needed in order to acquire fixed electric resistance, and the problem that the processability of a rubber constituent fell were also produced. Therefore,

although adding an ion conductivity grant agent to an ion conductive polymer or rubber, and adjusting the volume resistivity of rubber or polymer to the above-mentioned range also came to be made, and there is the advantage with little aging, it is easy to receive the environmental influence of the perimeters, such as temperature and humidity, and a volume-resistivity value is 102 easily. The problem which carries out degree change remains.

[0006]

[Problem(s) to be Solved by the Invention] This invention mainly solves said problem, and there are little dispersion and aging of electric resistance and it is offering a stable conductive polymer constituent also to fluctuation of an environmental condition moreover.

[0007]

[Means for Solving the Problem] In order to solve said problem, as a result of this invention persons inquire wholeheartedly, in a conductive polymer constituent which be make to distribute a very fine particle of a macromolecule (polymer A) which have ion conductivity in a small macromolecule (polymer B) of moisture permeability, and be obtain, it be hardly influenced to an environmental variation, and found out that the feature that little dispersion and aging of electric resistance which be the advantage of ion electric conduction be could be made to hold as it is.

[0008] Conductivity discovers this by very fine particle of a macromolecule (polymer A) which mainly has ion conductivity, and since there is little moisture permeability, a macromolecule which has separated these is considered that effect of moisture is because it hardly reaches at a very fine particle of a macromolecule which has ion conductivity. It consists of a macromolecule (polymer B) with little moisture permeability which forms a discontinuous phase and a sea phase of a very fine particle of a macromolecule (polymer A) which have ion conductivity, is added by Polymer B depending on conductivity which the polymer B itself has, and the case, it is mainly concerned with a conductive polymer constituent, and it can give conductivity sufficient as a whole by electronic conductivity grant agent.

[0009] However, in the whole conductivity which a conductive polymer constituent has, since there is demerit to which dispersion and aging of resistance become large under effect of a conductive bulking agent added when a conductive contribution of a small macromolecule (polymer B) of moisture permeability becomes large too much, a direction with many loadings of a macromolecule (polymer A) which has ion conductivity is desirable. Although 90 / 10 - 20/80 are specifically good as for a ratio of loadings (weight) of polymer A / polymer B, 80 / 20 - 50/50 are preferably [it is desirable and] good to 85 / 15 - 40/60, and a pan. If a macromolecule (polymer A) which has ion conductivity exceeds 90, it will become difficult to make it exist in stability as a discontinuous phase in a conductive polymer. Moreover, it is because effect of a macromolecule with little moisture permeability (polymer B) will become large too much if it becomes less than 20. It is most desirable for Polymer A to be 80-50, as mentioned above to stabilize conductivity by making a conductive subject of a conductive polymer constituent into ion conductivity.

[0010]

[Embodiment of the Invention] In order to distribute the macromolecule (polymer A) which has ion conductivity in a macromolecule with little moisture permeability (polymer B), the technique of dynamic vulcanization is used. If Polymer A and Polymer B are blended simply, since Polymer A will not necessarily become particle-like, therefore a part of continuous phase of Polymer A will come out to the surface and it will be greatly influenced of environmental variations, such as humidity, the effect of an environmental variation has been prevented using the technique of dynamic vulcanization. Moreover, as for the particle of Polymer A, it is desirable to make it distribute as most detailed possible particle. This is because electric resistance becomes easy to be stabilized, so that it distributes as a detailed particle.

[0011] While kneading Polymer A and Polymer B at the elevated temperature as generally well known about the method of dynamic vulcanization, it is the technique of carrying out differential powder into Polymer B, adding the chemical which makes Polymer A construct a bridge over the kneading object, and making Polymer A vulcanize. kneading — 100-250-degreeC — it is preferably carried out at about C 140-220-degree kneading temperature.

[0012] As for the size of the particle of the polymer A generated by dynamic vulcanization, it is preferably good that it is [50 micrometers or less / 20 micrometers or less] 10 micrometers or less still more preferably. If the grain size of Polymer A changes with the compatibility of Polymer A and Polymer B, the kneading method, and kneading temperature and especially compatibility becomes good, the grain size of Polymer A will become small. It is possible to adjust the addition of a compatibilizer and to adjust compatibility.

[0013] the macromolecule with which the macromolecule (polymer A) which has the ion conductivity of this invention can construct a bridge — it is — the volume resistivity of Polymer A — $RA^{**} - \log_{10} RA$ when carrying out It must be 12 or less. It has ion conductivity. As a macromolecule (polymer A) in which bridge formation like a parenthesis is possible Polyepichlorohydrin, a polyethylene oxide-epichlorohydrin copolymer (it is called Following ECO), An allyl-glycidyl-ether-ethyleneoxide-epichlorohydrin copolymer (it is called Following EGCO), An allyl-glycidyl-ether-polypropylene oxide-epichlorohydrin copolymer, An acrylonitrile-butadiene copolymer, polychloroprene, acrylic rubber, thermoplastic elastomer, such as rubber, such as polyurethane rubber, a styrene-isoprene-styrene block copolymer and this thing that carried out hydrogenation, styrene-Butadiene Styrene, and this thing that carried out hydrogenation, is independent — or it combines and is used suitably. Moreover, the polymer in which itself does not have ion conductivity can also be used as polymer A by adding an ion conductivity grant agent which is mentioned later.

[0014] Although it is required to choose the thing which makes Polymer A vulcanize as a vulcanizing agent used by this invention, and does not make Polymer B vulcanize, naturally the vulcanizing agent used according to the class of Polymer A and polymer B changes. In consideration of such a point, sulfur, sulfur content material, organic peroxide, and triazine can be used as a vulcanizing agent by this invention.

[0015] As sulfur content material, morpholine disulfide, alkylphenol disulfide, a macromolecule polysulfide, tetramethylthiuramdisulfide, etc. can be used. As organic peroxide, tertiarybutyl hydroperoxide, dicumyl peroxide, di-tertiary-butyl peroxide, n-butyl -4, 4-screw (tertiarybutyl peroxy) valerate, etc. can be used.

[0016] 2, 4, and 6-trimercapto-1,3,5-triazine etc. can be used as triazine. Furthermore, when a polyethylene oxide-epichlorohydrin copolymer is chosen as Polymer A and EPDM is chosen as Polymer B, as for the vulcanization system of Polymer A, specifically, it is desirable to use triazine.

[0017] In this invention, the vulcanization accelerator and vulcanization promotion assistant other than a vulcanizing agent can be used together as a vulcanization system chemical. As a vulcanization accelerator, although the various vulcanization accelerators of guanidine, thiourea, dithio carbamates, and thiurams can be used, diphenylguanidine, mercaptobenzothiazole, dibenzothiazyl disulfide, a tetraethylthiuram disulfide, etc. can more specifically be used.

[0018] As a vulcanization promotion assistant, a zinc oxide, a magnesium oxide, a minium, the white lead, stearin acid, oleic acid, triethanolamine, etc. can be used. As for the macromolecule with little moisture permeability (polymer B) used by this invention, it is good that the steam transmission coefficient P (g/cm·hr) for which it asked by the water permeability test is below 1.5×10^{-5} (g/cm·hr). The steam transmission coefficient P (g/cm·hr) has [the steam transmission coefficient P (g/cm·hr)] a more more desirable still value below 3.5×10^{-6} (g/cm·hr) the 5.5×10^{-6} to 6×10^{-6} (g/cm·hr) following preferably.

[0019] As polymer B, isobutylene isoprene rubber, halogenation isobutylene isoprene rubber, the bromination object of the copolymer of alkyl styrene and an isobutylene, Ethylene propylene rubber and its denaturation object, an ethylene-propylene-diene copolymer (EPDM), Chlorinated polyethylene (CPE), chlorosulfonated polyethylene, a styrene butadiene rubber, Rubber, such as polyisoprene, poly polynorbornene rubber, and polychloroprene, And polyethylene, polypropylene, nylon, urethane, polyvinyl chloride, Although thermoplastics, such as a poly vinylidene chloride, polycarbonate, and styrene-isoprene-styrene copolymer and this hydrogenation object, styrene-Butadiene Styrene, and this hydrogenation object, can use it suitably Also especially in this, isobutylene isoprene rubber, halogenation isobutylene isoprene rubber, the bromination object of the copolymer of alkyl styrene and an isobutylene, ethylene propylene rubber, and an ethylene-

propylene-diene copolymer have the low transmission coefficient of a steam, and it is desirable. [0020] When thermoplastics is used as polymer B, after dynamic vulcanization, conductive grant material is added if needed, a conductive polymer constituent is obtained, it can fabricate after that and a product can be obtained. As conductive grant material, carbon black, a metal powder, a cation system surfactant, quarternary ammonium salt, and fatty acid ester can be used.

[0021] Moreover, when rubber is used as polymer B, after dynamic vulcanization of Polymer A, conductive grant material can be added if needed, the vulcanization system chemical over which Polymer B is made to construct a bridge further can be added, a conductive polymer constituent can be obtained after kneading, and a conductive part can be obtained the postforming and by pressing. In this invention, it is also possible to add an ion conductivity grant agent if needed. The plasticizer which dissolved or blended ion conductivity material like lithium perchlorate as an ion conductivity grant agent, oligomer, resin, etc. are mentioned. As a concrete example of an ion conductivity grant agent, US70 ** 2 made from 3 vatting ***** of a type and the SUMIEDO 600 grade by Sumitomo Chemical Co., Ltd. which dissolved ion conductivity material are mentioned. US70 ** 2 uses a plasticizer as the base, and SUMIEDO is the object which made the oligomer of the polyethylene structure of having a polyoxyethylene in a side chain contain lithium perchlorate.

[0022] Former one is desirable, although an ion conductivity grant agent can also be beforehand blended with Polymer A before dynamic vulcanization and it can also blend to Polymer A, Polymer B, and coincidence at the time of dynamic vulcanization. The addition of an ion conductivity grant agent is added so that Polymer A may have desirable conductivity. 50 or less phrs of 30 or less phrs of additions are 20 or less phrs more preferably about an ion conductivity grant agent to polymer A100phr. It is because there is a possibility of carrying out bleeding by the case when many [too].

[0023] As an ion conductivity grant agent, besides lithium perchlorate, a lithium chloride (LiCl), A lithium bromide (LiBr), a lithium iodide (LiI), a lithium nitrate (LiNO₃), A thiocyanic acid lithium (LiSCN), a sodium thiocyanate (NaSCN), Trifluoromethyl lithium sulfate (LiSO₃ CF₃), a sodium bromide (NaBr), A sodium iodide (NaI), a sodium thiocyanate (NaSCN), A sodium perchlorate (NaClO₄), a trifluoromethyl sodium sulfate (NaSO₃ CF₃), Potassium iodide (KI), a potassium thiocyanate (KSCN), a potassium perchlorate (KClO₄), etc. these zinc salt, a calcium salt, magnesium salt, etc. can be used.

[0024] The conductivity of the blend object of Polymer A or Polymer A, and an ion conductivity grant agent needs to be 10³–10¹¹, if it takes into consideration using for the conductive part for copying machines as mentioned above for example. In order that this may combine with the polymer B in which conductivity is inferior, it is because it asks that an ion conductive polymer portion has more high conductivity.

[0025] On the other hand, when the conductivity of Polymer B is too low, there is a trouble that the conductivity as the whole becomes low. Conversely, when the conductivity of Polymer B becomes higher than Polymer A, the electrical and electric equipment has the problem to which dispersion in aging or electric resistance becomes large in order to mainly pass Polymer B. Therefore, the conductivity of Polymer B needs to be in level somewhat lower than the conductivity of Polymer A. Specifically, it is resistance log₁₀RA of Polymer A. Resistance log₁₀RB of Polymer B It is desirable for a difference to be less than five, and it is more desirable that it is less than three. That is, it is RB about RA and the volume resistivity value of Polymer B in the volume resistivity value of Polymer A. Carry out. [Equation 1]

$$0 < -\text{Log}_{10}\text{RB} - \text{Log}_{10}\text{RA} \leq 5 \quad (1)$$

It is desirable that it is satisfied.

[0026] For giving such conductivity to Polymer B, it is desirable to add electronic conductivity grant material to Polymer B. As electronic conductivity grant material, carbon black is mainly used. Also in carbon black, conductive high acetylene black can use it suitably especially. Although it is necessary to determine the amount of electronic conductivity grant material according to conductivity to which the aforementioned (1) formula is satisfied, it is less than 50 phrs preferably less than 100 phrs to polymer B100phr.

[0027] As for electronic conduction nature grant material, it is desirable to make it distribute

mainly in Polymer B. Therefore, after Polymer A fully distributes and vulcanizes in Polymer B at the time of dynamic vulcanization, it is desirable to add electronic conduction nature grant material. Polymer A understands having fully distributed and having vulcanized in Polymer B, by observing the torque which kneading at the time of dynamic vulcanization takes. That is, although rubber is plasticized and torque decreases at the beginning of kneading, if Polymer A distributes in Polymer B after that and vulcanization progresses, the torque which kneading takes will begin increase and will become the maximum. Into the polymer A vulcanized even if it added carbon black, after passing over this point, carbon black stops being able to enter easily, and it mainly comes to distribute to Polymer B. In contrast, when carbon black is supplied from the time of kneading, carbon enters not only into polymer B but into polymer A at a remarkable rate, Polymer A has electronic conduction nature and there is a possibility [**** / that dispersion in electric resistance becomes large] of receiving aging. Moreover, there is also a possibility that it may become impossible to give electronic conductivity required for Polymer B. [0028] In addition, when the compatibility of Polymer A and Polymer B is too low, Polymer A does not distribute well in Polymer B, but conductivity becomes unstable. Therefore, it is necessary to raise the compatibility between Polymer A and Polymer B, and Polymer A needs to carry out differential powder into Polymer B. It is the solubility parameter usually used, i.e., SP value, (it is simple to use an unit: $[\text{cal}^{1/2} \cdot \text{cc}^{-1/2}]$.) to investigate the compatibility of Polymer A and Polymer B. In a certain case, a problem may come out [the difference of SP value of Polymer A and Polymer B] to compatibility two or more. In such a case, it is good to add material which has both the components of Polymer A and Polymer B in a monad, or material with SP value between Polymer A and Polymer B at the time of dynamic vulcanization. Thus, the material which improves the compatibility of Polymer A and Polymer B is called a compatibilizer. When the difference of SP value adds a compatibilizer two or more in a certain case, and there is no compatibilizer, differential powder also of the system which does not have Polymer A a differential handbill into Polymer B can be carried out, and it can maintain conductivity at stability and fitness.

[0029] Although the compatibilizer to be used naturally changes according to the class of Polymer A and polymer B, the 30 or less phrs of the amount of the compatibilizer used are 20 or less phrs preferably about to a total of 100 phrs of Polymer A and Polymer B. a compatibilizer — one kind — or two or more kinds can be used. case the difference of SP value of Polymer A and Polymer B is large — a compatibilizer — for example, — if two sorts are used — the difference of SP value of Polymer A and a compatibilizer 1 — less than two — moreover, while being able to attain the whole compatibility-ization by making the difference of SP value of a compatibilizer 1 and a compatibilizer 2 less than into two, and making the difference of SP value of a compatibilizer 2 and Polymer B less than into two, the amount of the whole compatibilizer can be reduced.

[0030] Inorganic pigments, organic pigments, etc., such as plasticizers, such as softeners, such as bulking agents, such as an antioxidant, a silica, clay, and a calcium carbonate, and a mineral oil, dioctyl phthalate (DOP), and dioctyl adipate (DOA), titanium oxide, and red ocher, can be added if needed to Polymer A and/, or Polymer B other than these.

[0031]

[Example] An example and the example of a comparison are given to below, and this invention is explained still more concretely. This invention is not limited to the following examples, unless the summary is exceeded.

It blended with the loadings which show one to examples 1–8 and example of comparison 8 polymer A, Polymer B, and various compounding agents in tables 1–4. The unit of loadings is the weight section.

[0032] It is shown that a, b, c, and d which were indicated in the column of the processing method in a table 1, a table 2, a table 3, and a table 4 carried out kneading processing using the following method.

a: Set laying temperature of a kneading machine to about 180-degreeC, kneading the masterbatch A containing Polymer A, and the masterbatch B containing Polymer B, add the chemical which makes Polymer A vulcanize and make Polymer A vulcanize dynamically. Then,

the vulcanizing agent and additive of final kneading are added, that which kneaded by about 100-degreeC is taken out from a kneading machine, and it fabricates with a press.

[0033] b: Set laying temperature of a kneading machine to about 140-degreeC, kneading the masterbatch A containing Polymer A, and the masterbatch B containing Polymer B, add the chemical which makes Polymer A vulcanize and make Polymer A vulcanize dynamically. Then, the additive of final kneading is added, that which kneaded by about 100-degreeC is taken out from a kneading machine, and it fabricates with a press.

[0034] c: Once take out from a kneading machine and cool, after setting laying temperature of a kneading machine to about 180-degreeC and carrying out the mastication of the masterbatch A. Then, that which added the vulcanizing agent by the kneading inside of a plane, and kneaded by about 100-degreeC is taken out, and it fabricates with a press.

d: Set laying temperature of a kneading machine to about 180-degreeC, and knead Masterbatch A and Masterbatch B. Then, that which added the vulcanizing agent by the kneading inside of a plane, and kneaded by about 100-degreeC is taken out, and it fabricates with a press.

Moreover, although notes were attached with a table 1 – a table 4, it is as follows for details.

[0035]

[A table 1]

	実施例 1	実施例 2	実施例 3	実施例 4
マスターバッチ A				
ポリマー A 1 *1	—	8.0	8.0	8.0
ポリマー A 2 *2	5.0	—	—	—
イオン導電性付与剤 1 *3	—	—	4.0	—
イオン導電性付与剤 2 *4	—	—	—	5.0
相溶化剤 1 *5	7.5	12.0	4.0	12.0
相溶化剤 2 *6	—	—	—	—
界面活性剤 1 *7	—	—	—	—
受酸剤 1 *8	8.6	—	—	—
受酸剤 2 *25	—	8.0	8.0	8.0
マスターバッチ B				
ポリマー B 1 *9	5.0	—	—	—
ポリマー B 2 *10	—	2.0	2.0	2.0
ポリマー B 3 *11	—	—	—	—
ポリマー B 4 *26	—	—	—	—
相溶化剤 1	7.5	3.0	2.0	3.0
相溶化剤 3 *12	—	—	—	—
界面活性剤 1	—	—	—	—
受酸剤 1	1.1	—	—	—
受酸剤 2	—	—	—	—
動的加硫用添加剤				
加硫促進剤 1 *13	0.8	—	—	—
加硫促進剤 2 *14	0.8	0.4	0.4	0.4
加工助剤 *15	1.0	1.0	1.0	1.0
亜鉛華 *19	—	—	—	—
加硫剤 1 *16	0.8	—	—	—
加硫剤 2 *17	—	0.7	0.7	0.7
ファイナル練り用添加剤				
導電性充填剤 1 *18	1.1	5	6	5
加工助剤	1.0	1.0	1.0	1.0
亜鉛華	2.5	1.0	1.0	1.0
加硫促進剤 3 *20	0.5	—	—	—
加硫促進剤 4 *21	—	0.2	0.2	0.2
加硫剤 3 *23	—	0.2	0.2	0.2
加工方法	a	a	a	a

[0036]

[A table 2]

	実施例 5	実施例 6	実施例 7	実施例 8
マスターバッチ A				
ポリマー A 1	8 0	—	—	5 0
ポリマー A 2	—	5 0	5 0	—
イオン導電性付与剤 1	—	—	—	—
イオン導電性付与剤 2	—	—	—	—
相溶化剤 1	1 2. 0	—	—	—
相溶化剤 2	—	3. 0	—	—
界面活性剤 1	—	—	1. 0	—
受酸剤 1	—	8. 0	7. 5	—
受酸剤 2	8. 0	—	—	5. 0
マスターバッチ B				
ポリマー B 1	—	5 0	5 0	—
ポリマー B 2	—	—	—	—
ポリマー B 3	2 0	—	—	—
ポリマー B 4	—	—	—	5 0
相溶化剤 1	3. 0	—	—	—
相溶化剤 3	—	3. 0	—	—
界面活性剤 1	—	—	1. 0	—
受酸剤 1	—	0. 5	—	—
受酸剤 2	—	—	—	5. 0
動的加硫用添加剤				
加硫促進剤 1	—	0. 8	0. 8	0. 8
加硫促進剤 2	0. 4	0. 8	0. 8	0. 8
加工助剤	1. 0	1. 0	1. 0	1. 0
亜鉛華	—	—	—	2. 5
加硫剤 1	—	0. 8	0. 8	0. 8
加硫剤 2	0. 7	—	—	—
ファイナル練り用添加剤				
導電性充填剤 1	5	1 1	1 1	1 1
加工助剤	1. 0	1. 0	1. 0	1. 0
亜鉛華	—	2. 5	2. 5	—
加硫促進剤 3	—	0. 5	0. 5	—
加硫促進剤 4	—	—	—	—
加硫剤 3	—	—	—	—
加工方法	a	a	a	b

[0037]

[A table 3]

	比較例 1	比較例 2	比較例 3	比較例 4
マスターバッチ A				
ポリマー A 1	1 0 0	1 0 0	—	—
ポリマー A 2	—	—	—	5 0
ポリマー A 3 *28	—	—	—	—
イオン導電性付与剤 1	—	5. 0	—	—
イオン導電性付与剤 2	—	—	—	—
相溶化剤 1	—	—	—	7. 5
相溶化剤 2	—	—	—	—
受酸剤 1	—	—	—	8. 6
受酸剤 2	1 0	1 0	—	—
導電性充填剤 2 *29	—	—	—	—
マスターバッチ B				
ポリマー B 1	—	—	1 0 0	5 0
ポリマー B 2	—	—	—	—
ポリマー B 5 *30	—	—	—	—
相溶化剤 1	—	—	—	7. 5
受酸剤 1	—	—	—	1. 1
受酸剤 2	—	—	—	—
動的加硫用添加剤				
加硫促進剤 1	—	—	—	—
加硫促進剤 2	—	—	—	—
加硫促進剤 6 *31	—	—	—	—
加工助剤	—	—	—	—
亜鉛華	—	—	—	—
加硫剤 1	—	—	—	—
加硫剤 2	—	—	—	—
ファイナル練り用添加剤				
導電性充填剤 1	—	—	2 3	2 0
加工助剤	1. 0	1. 0	1. 0	1. 0
亜鉛華	5. 0	5. 0	5. 0	5. 0
加硫促進剤 3	—	—	1. 0	0. 5
加硫促進剤 4	—	—	—	—
加硫促進剤 5 *22	1. 5	1. 5	—	0. 8
加硫促進剤 7 *32	1. 5	1. 5	—	0. 8
加硫剤 3	1. 5	1. 5	—	0. 8
加硫剤 4 *24	—	—	—	—
加工方法	c	c	c	d

[0038]

[A table 4]

	比較例 5	比較例 6	比較例 7	比較例 8
マスターバッチ A				
ポリマー A 1	—	—	5 0	—
ポリマー A 2	5 0	2 0	—	—
ポリマー A 3	—	—	—	5 0
イオン導電性付与剤 1	—	—	—	—
イオン導電性付与剤 2	—	—	—	—
相溶化剤 1	7. 5	3. 0	—	—
相溶化剤 2	—	—	—	—
受酸剤 1	8. 6	3. 5	—	—
受酸剤 2	—	—	5. 0	—
導電性充填剤 2	—	—	—	1 2
マスターバッチ B				
ポリマー B 1	5 0	8 0	—	—
ポリマー B 2	—	—	—	5 0
ポリマー B 5	—	—	5 0	—
相溶化剤 1	7. 5	3. 0	—	—
受酸剤 1	1. 1	—	—	—
受酸剤 2	—	—	5. 0	—
動的加硫用添加剤				
加硫促進剤 1	0. 8	0. 3	0. 8	—
加硫促進剤 2	0. 8	0. 3	0. 8	—
加硫促進剤 6	—	—	—	0. 5
加工助剤	1. 0	1. 0	1. 0	1. 0
亜鉛華	—	—	2. 5	2. 5
加硫剤 1	0. 8	0. 3	0. 8	—
加硫剤 2	—	—	—	—
ファイナル練り用添加剤				
導電性充填剤 1	1 3	—	—	1 1
加工助剤	—	1. 0	1. 0	1. 0
亜鉛華	2. 5	4. 0	4. 0	2. 5
加硫促進剤 3	0. 5	0. 8	—	—
加硫促進剤 4	—	—	0. 2	0. 5
加硫促進剤 5	—	—	—	—
加硫促進剤 7	—	—	1. 2	—
加硫剤 3	—	—	—	0. 5
加硫剤 4	—	—	0. 5	—
加工方法	a	a	b	b

[0039] *1: EPIKUROMA CG 102 by DAISO Co., Ltd. which is EGCO as polymer A1 was used. It is the SP value 11 and log10RA1 when setting volume resistivity to RA1 is 8.2.

*2: EPIKUROMA CG by DAISO Co., Ltd. which is EGCO as polymer A2 was used. *3 whose log10RA2 when setting volume resistivity to RA2 it is the SP value 11 and is 8.5: It presupposed that it is an ion conductivity grant agent 1, and SUMIEDO 600 by Sumitomo Chemical Co., Ltd. was used. (Oligomer)

*4: US-70 ** 2 made from 3 vatting ***** was used as an ion conductivity grant agent 2. (Plasticizer)

*5: The DAISO rack RA 140 by DAISO Co., Ltd. which is chlorinated polyethylene (CPE) as a

compatibilizer 1 was used. SP value is 9.1. It can be used as polymer B and CPE can be used also as a compatibilizer.

[0040] *6: The DAISO rack G245 by DAISO Co., Ltd. which is chlorinated polyethylene (CPE) as a compatibilizer 2 was used. It is the SP value 9.3. It can be used as polymer B and CPE can be used also as a compatibilizer.

*7: Nonion system surfactant AKUCHI Norian C-5 by Matsumoto fats-and-oils incorporated company was used as a surfactant.

[0041] *8: The precipitated calcium carbonate by Maruo Calcium Co., Ltd. was used as carrier acid 1.

*9: EXXPRO by Exxon Chemistry Incorporated company which is the bromination object of the copolymer of alkyl styrene and an isobutylene as polymer B1 MDX 90-10 was used. SP value is 7.7 and the steam transmission coefficient for which it asked by the water permeability test is 5×10^{-7} g/cm-hr.

[0042] *10: S PUREN 553 by Sumitomo Chemical Co., Ltd. which is EPDM as polymer B-2 was used. SP value is 8 and the steam transmission coefficient for which it asked by the water permeability test is 3.1×10^{-6} g/cm-hr.

*11: SEPUTON 2002 by Kuraray Co., Ltd. which is a styrene thermoplastic elastomer (TPE) as polymer B3 was used. SP value is 8 and the steam transmission coefficient for which it asked by the water permeability test is 5×10^{-6} g/cm-hr.

[0043] *12: As a compatibilizer 3 ERASUREN TR by Showa Denko K.K. which is chlorinated polyethylene (CPE) was used. SP value is 8.6.

*13: Trade name Nocceler DM was used by the dibenzothiazyl disulfide by Ouchi Shinko Chemical Industries as a vulcanization accelerator 1 for dynamic vulcanization.

*14: Trade name Nocceler TS was used by the tetramethylthiurammonosulfide by Ouchi Shinko Chemical Industries as a vulcanization accelerator 2 for dynamic vulcanization.

[0044] *15: Uniqema Australia 4931 which is stearin acid as processing aid was used.

*16: The powder sulfur by the Tsurumi Chemistry Company was used as a vulcanizing agent 1 at the time of dynamic vulcanization.

*17: Trade name OF-100 were used by 2 by DAISO Co., Ltd., 4, and 6-trimercapto-1,3,5-triazine as a vulcanizing agent 2 at the time of dynamic vulcanization.

[0045] *18: the acetylene black by DENKI KAGAKU KOGYO K.K. as a conductive bulking agent 1 added by final kneading — trade name DIN — a turnip — the rack was used.

*19: The zinc white No. 1 by Toho Zinc Co., Ltd. was used. A zinc white is EXXPRO blended with an example 1, an example 6, an example 7, the example 3 of a comparison, the example 4 of a comparison, the example 5 of a comparison, the example 6 of a comparison, and the example 8 of a comparison. To MDX 90-10, it is blended with stearin acid, acts as a vulcanizing agent, and, in the case of others, acts as a vulcanization promotion assistant.

[0046] *20: Trade name Nocceler TRA was used by the dipentamethylenethiuramtetrasulfide by Ouchi Shinko Chemical Industries as a vulcanization accelerator 3 added by final kneading.

*21: Trade name Nocceler BZ was used with the zinc dibutyldithiocarbamate made from the Ouchi Shinko Chemical industry as a vulcanization accelerator 4 added by final kneading.

[0047] *22: Trade name Nocceler TS was used by the tetramethylthiurammonosulfide by Ouchi Shinko Chemical Industries as a vulcanization accelerator 5 added by final kneading.

*23: The powder sulfur by the Tsurumi Chemistry Company was used as a vulcanizing agent 3 added by final kneading.

[0048] *24: Trade name OF-100 were used by 2 by DAISO Co., Ltd., 4, and 6-trimercapto-1,3,5-triazine as a vulcanizing agent 4 added by final kneading.

*25: DHT-4A-2 which are an aluminum chloride magnesium carbonate hydrate made from consonance chemistry as carrier acid 2 were used.

[0049] *26: The DAISO Co., Ltd. make G235 which is chlorinated polyethylene (CPE) as polymer B4 was used. SP value is 8.9 and the steam transmission coefficient for which it asked by the water permeability test is 5×10^{-6} g/cm-hr.

*28: EXXPRO by Exxon Chemistry Incorporated company which is the bromination object of the copolymer of PARAME chill styrene and an isobutylene as polymer A3 MDX 90-10 was used. SP

value is 7.7, and log10RA 3 when setting volume resistivity at the time of adding acetylene black to RA 3 are 6.6 as shown in the masterbatch A of the example 8 of a comparison.

[0050] *29: the acetylene black by DENKI KAGAKU KOGYO K.K. as a conductive bulking agent 2 added to Polymer A — trade name DIN — a turnip — the rack was used.

*30: EPIKUROMA H by DAISO Co., Ltd. which is a polyethylene oxide-EPIKUROHI drine compounds copolymer (ECO) as polymer B5 was used. SP value is 10 and the steam transmission coefficient for which it asked by the water permeability test is 3.5×10^{-5} g/cm-hr.

[0051] *31: Trade name Nocceler EZ was used with the zinc diethyldithiocarbamate by Ouchi Shinko Chemical Industries as a vulcanization accelerator 6 for dynamic vulcanization.

*32: Trade name Nocceler DM was used by the dibenzothiazyl disulfide by Ouchi Shinko Chemical Industries as a vulcanization accelerator 7 added by final kneading.

The macromolecule constituent of this invention was kneaded with incorporated company Oriental energy machine factory 250ml small Banbury mold lab PURASUTO mill.

[0052] After it adjusted ***** to a predetermined temperature and it performed the mastication under high-speed rotation of 100rpm for 2 to 3 minutes, it was performed necessity time. It decided on this time amount by observing the torque which kneading takes as stated previously. In addition, ***** was performed after producing the masterbatch A containing them, or Masterbatch B by kneading using the opening-roll etc. beforehand, when you needed a compatibilizer, a surfactant, an ion conductivity grant agent, carrier acid, etc.

[0053] After fabricating the ***** constituent obtained as mentioned above, the press-forming machine performed the optimal time amount press at proper temperature. After the press, after grinding the surface and making it 2mm thickness, the volume resistivity R of a conductive polymer constituent was measured, and it asked for volume resistivity value log10R. The evaluation result of each example and the example of a comparison was shown in a table 5, a table 6, a table 7, and a table 8.

[0054] In addition, if needed, after grinding the rubber thickness after polishing so that it may be set to 0.50 ± 0.05 mm when using as an imprint belt, it applies and coat agents, such as urethane resin, are calcinated so that thickness may be set to about 10 micrometers. It is the volume resistivity value R0 as a product which also includes the coat layer when giving a coat layer although the same was said of the transfer roller to accept necessity, and to apply and calcinate a coat agent. It is desirable to be set to 104–1012 (ohm-cm) which was described previously.

[0055] When the coat layer by about 10-micrometer urethane resin system coat agent is generally prepared, by the imprint belt of the 0.50 ± 0.05 mm of the above-mentioned rubber thickness, the volume resistivity as a product goes up about the about 0.5 to 1st power.

[0056] 1) Measurement of the measuring method volume resistivity value R of the volume resistivity value R (ohm-cm) is JIS. It carried out based on the measuring method of a volume resistivity given in K6911 "the thermosetting plastic commercial-test method." Volume resistivity log10R was computed about the obtained sample. The measuring method of dispersion in volume resistivity, aging, and an environmental dependency is as follows.

2) Prepare respectively eight samples obtained in dispersion each example and the example of a comparison of volume resistivity, measure the volume resistivity of eight samples each, and it is difference $\Delta \log_{10} R_1$ of the maximum and minimum value. It asked. Dispersion in volume resistivity will be large, so that this difference is large.

3) It prepared at a time eight samples obtained in aging each example and the example of a comparison of volume resistivity, and was left for four weeks under the room temperature. And the volume resistivity of each sample is measured a total of 5 times immediately after a sampling and of one week, two weeks, three weeks, and four weeks after, the average of eight pieces each for every example and example of a comparison is calculated at each time, and it is difference $\Delta \log_{10} R_2$ of the maximum of this average, and the minimum value. It asked and the average of eight samples was calculated. Aging of volume resistivity will be large, so that this difference is large.

4) Difference $\Delta \log_{10} R_3$ of the two averages which left at a time eight samples obtained in each example and the example of a comparison for 24 hours, respectively, calculated the average of the volume resistivity under each environment, and were acquired under [of the

environmental dependency temperature C of 10 degrees of volume resistivity, and 15% of relative humidity] environment and the environment of the temperature C of 32.5 degrees, and 90% of relative humidity It asked.

5) Leave the measuring method sample of bleeding nature for one week under the ambient atmosphere of 55% of humidity at the temperature C of 23 degrees, using viewing, tactile feeling, and a filter paper, divide into the following three-stage whether the liquefied blot has appeared in the material-list side, and evaluate it.

[0057]

x: It is the time when it can check that bleed in **:viewing, and a broth is not checked, but touch by hand, and stickiness is not sensed when a blot broth is checked visually, or when it touches by the hand and stickiness is sensed, but liquefied objects, such as an ion conductivity grant agent, will have shifted to the filter paper if a filter paper is applied and rubbed to a sample.

[0058] O : it is a time of bleeding visually and a broth not being checked, and it not being checked that the liquefied object has shifted to the filter paper, even if it touches by hand, and stickiness is not sensed but it applies and rubs a filter paper to a sample further.

6) log10RA And log10RB log10RA in measuring method each example and the example of a comparison Or log10RB It created and asked for the sample as follows.

[0059] The press-forming machine performed the optimal time amount press for the constituent which added the vulcanization accelerator for dynamic vulcanization, a vulcanizing agent, and processing aid with the below-mentioned loadings to the constituent of Masterbatch A, and was kneaded and obtained at proper temperature. It is RA, after grinding the surface after a press and making it 2mm thickness. It measures and is volume resistivity value log10RA. It asked. In addition, the loadings of the vulcanization accelerator for dynamic vulcanization, a vulcanizing agent, and processing aid added the amount which made it negotiate with each loadings of these additives shown in tables 1-4 about the weight ratio of the /polymer A in each example or the example of a comparison (polymer A+ polymer B).

[0060] The press-forming machine performed the optimal time amount press for the constituent which added the conductive bulking agent agent for final kneading, the assistant (zinc white), the vulcanizing agent, and the vulcanization accelerator with the below-mentioned loadings to the constituent of Masterbatch B, and was kneaded and obtained at proper temperature. It is RB, after grinding the surface after a press and making it 2mm thickness. It measures and is volume resistivity value log10RB. It asked. In addition, the loadings of the conductive bulking agent agent for final kneading, an assistant (zinc white), a vulcanizing agent, and a vulcanization accelerator added the amount which multiplied the weight ratio of the /polymer B in each example or the example of a comparison (polymer A+ polymer B) by each loadings behind these additives shown in tables 1-4.

7) The steam transmission coefficient P of the measuring method polymer B of the steam transmission coefficient P (g/cm, hr) is JIS. It is the moisture vapor transmission M (g/m² and 24hr) for which it asked based on Z0208 1 hour and a moisture permeation area of 1cm by (2) types 2 And it is the value which converted into per thickness of 1cm of a test piece, and was acquired. Namely, when referred to as thickness [of a test piece] T (cm) [0061]

[Equation 2]

$$P=M/(24 \times 10000 \times T) \quad (2)$$

It is alike and is computed more.

[0062]

[A table 5]

	実施例 1	実施例 2	実施例 3	実施例 4
ブリード性	○	○	○	○
ポリマー A の $\log_{10} R_A$	8.6	8.2	6.6	7.0
ポリマー B の $\log_{10} R_B$	8.9	8.5	7.5	8.5
導電性高分子組成物の $\log_{10} R$	8.7	8.3	6.8	7.3
体積固有抵抗のばらつき $\Delta \log_{10} R_1$	0.3	0.2	0.2	0.2
体積固有抵抗の経時変化 $\Delta \log_{10} R_2$	0.2	0.2	0.4	0.3
体積固有抵抗の環境依存性 $\Delta \log_{10} R_3$	0.2	0.4	0.5	0.4

[0063]

[A table 6]

	実施例 5	実施例 6	実施例 7	実施例 8
ブリード性	○	○	○	○
ポリマー A の $\log_{10} R_A$	8.2	8.5	8.5	8.2
ポリマー B の $\log_{10} R_B$	8.6	8.9	8.9	8.8
導電性高分子組成物の $\log_{10} R$	8.3	8.7	8.7	8.5
体積固有抵抗のばらつき $\Delta \log_{10} R_1$	0.3	0.3	0.3	0.2
体積固有抵抗の経時変化 $\Delta \log_{10} R_2$	0.3	0.3	0.3	0.2
体積固有抵抗の環境依存性 $\Delta \log_{10} R_3$	0.4	0.1	0.2	0.3

[0064]

[A table 7]

	比較例 1	比較例 2	比較例 3	比較例 4
ブリード性	○	△	○	○
ポリマー A の $\log_{10} R_A$	8.2	6.6	—	—
ポリマー B の $\log_{10} R_B$	—	—	8.5	—
導電性高分子組成物の $\log_{10} R$	8.2	6.6	8.5	6.4
体積固有抵抗のばらつき $\Delta \log_{10} R_1$	0.1	0.2	1.5	1.6
体積固有抵抗の経時変化 $\Delta \log_{10} R_2$	0.3	0.3	0.8	0.9
体積固有抵抗の環境依存性 $\Delta \log_{10} R_3$	1.5	1.9	0.1	0.3

[0065]

[A table 8]

	比較例 5	比較例 6	比較例 7	比較例 8
ブリード性	○	○	○	○
ポリマー A の $\log_{10} R_A$	8.6	8.6	8.2	8.5
ポリマー B の $\log_{10} R_B$	7.5	14.0	10.0	9.2
導電性高分子組成物の $\log_{10} R$	7.6	13.1	9.1	8.8
体積固有抵抗のばらつき $\Delta \log_{10} R_1$	1.6	0.3	0.1	1.6
体積固有抵抗の経時変化 $\Delta \log_{10} R_2$	0.8	0.2	0.2	1.0
体積固有抵抗の環境依存性 $\Delta \log_{10} R_3$	0.1	1.1	1.7	0.2

[0066]

[Effect of the Invention] The conductive polymer constituent with little aging whose electric resistance had few environmental dependencies by distributing Polymer A in Polymer B and making it vulcanize with dynamic vulcanization, and was stable in the polymer A which has ion conductivity, and polymer B with little moisture permeability can be obtained.

[Translation done.]

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(54) 【発明の名称】 導電性高分子組成物およびそれを用いた導電性部品

(57) 【要約】

【課題】 電気抵抗のばらつきや経時変化が少なく、しかも環境条件の変動に対しても安定な導電性高分子組成物または導電性部品を提供すること。

【解決手段】 イオン導電性を有する高分子と導電性の少ない高分子からなる導電性高分子組成物であって、イオン導電性を有する高分子は動的加減にしたことを前提とし、導電性の少ない高分子を連続相としたことを特徴とする導電性高分子組成物または前記高分子組成物を用いた導電性部品

(2)

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2

【発明の要約】

【請求項1】 イオン導電性を有する高分子であるポリマーAと導電性の少ない高分子であるポリマーBからなる導電性高分子組成物であって、ポリマーAは動的加減により粒状の不連続相とし、ポリマーBを連続相としたことを特徴とする導電性高分子組成物

【請求項2】 イオン導電性を有する高分子であるポリマーAと導電性の少ない高分子であるポリマーBからなる導電性高分子組成物であって、ポリマーAは動的加減により粒状の不連続相とし、ポリマーBを連続相とした導電性高分子組成物を用いたことを特徴とする導電性部品

【発明の詳細な説明】

【0001】
【発明の属する技術分野】 本発明は導電性高分子組成物に関し、特に複写機等の感光体まわりの導電性部品、すなわち帯電ローラー、転写ベルト、転写ローラー等に好適な導電性高分子組成物に関するものである。

【0002】
【従来の技術】 従来から、たとえば複写機、レーザープリンター、普通紙ファクシミリなどの電子写真装置においては、印刷紙を感光体に接触させてトナーを転写させるとともに、静電力によって印刷紙を搬送する転写ベルトが使用されている。かかる転写ベルトを用いると、印刷紙の種類や搬送速度などの影響を比較的に受けずに、トナー像の転写を良好に行うことができ、かつ、転写後の印刷紙を強制的に感光体から分離させて、保持、搬送することができ。

【0003】 この他、別に搬送ベルトを用い、それによって搬送されてきた印刷紙をトナー像を形成した感光体の表面に接触させてトナー像を印刷紙の表面に転写させる転写ローラーやトナーを感光体に吸着させるために感光体に接触回転して電荷を与える帯電ローラーが知られている。転写ベルト、転写ローラー、帯電ローラー等は体積固有抵抗が $10^4 \sim 10^{12} \Omega \cdot \text{cm}$ 程度の導電性を有して、電荷の移動を容易にする必要がある。転写ベルトの場合、体積固有抵抗が上記の範囲を下回ると、リーク、紙汚れなどの画像上の問題が発生する。一方、体積固有抵抗が上記の範囲を超える場合、転写効率が悪く、美用に達しない。転写ローラーや帯電ローラーの場合も上記の電気抵抗範囲からはずれると同様に問題が生じる。

【0004】 そこで従来は、基材ゴムに電子導電性付与剤であるカーボンブラックを配合した導電性のゴム組成物から形成された導電性ベルトが、転写ベルトとして用いられていた。転写ローラーや帯電ローラーも同様である。ところが、上記のごとき電子導電性付与剤を添加して導電性を調節した場合、言い換えれば電子導電性付与剤による電子伝導のみでゴムに導電性を付与した場合には、当該電子導電性付与剤の配合量のわずかな変化や、電子導電性付与剤の分散状態によって電気抵抗が大きくばらついた、導電性が経時的に不安定になったりするなどの

の問題が生じ、かかる構成の導電性ベルトを転写ベルトとして、また、かかる構成の導電性ローラーを転写ローラーや帯電ローラーとして使用して印刷を行っても、安定した画像が得られないうえに、転写不良が生じた。

【0005】 また、電子導電性付与剤の添加量が多くなれば、電気抵抗の印刷電圧への依存性が大きくなり、一定の電気抵抗を得るために精密な印刷電圧制御装置が必要になるという問題や、ゴム組成物の加工性が低下するという問題も生じた。そのため、イオン導電性ポリマーもしくはゴムにイオン導電性付与剤を添加して、ゴムやポリマーの体積固有抵抗を前述の範囲に調整することもなされるようになったが、経時変化が少ない長所はあるが、湿度や温度といった周囲の環境の影響を受けやすく、容易に体積抵抗値が 10^2 程度変化してしまいう問題が残っている。

【0006】
【発明が解決しようとする課題】 本発明は、主に前記問題を解決して、電気抵抗のばらつきや経時変化が少なく、しかも環境条件の変動に対しても安定な導電性高分子組成物を提供することである。

【0007】

【課題を解決するための手段】 前記問題を解決するため、本発明者は、導電性高分子の微細粒子を導電性の小さい高分子（ポリマーA）の中に分散させて得られる導電性高分子（ポリマーB）に対して、環境変動に対して影響をほとんど受けないイオン導電の長所である電気抵抗のばらつきや経時変化が少なくという特徴をそのまま保持させることができることを見出した。

【0008】 これは、導電性が主としてイオン導電性を有する高分子（ポリマーA）の微細粒子により実現し、これらを隔てている高分子の微細粒子に少ない影響をほとんど導電性を有する高分子の微細粒子に水分の影響がほとんど及ばないことによると考えられる。導電性高分子組成物は、イオン導電性を有する高分子（ポリマーA）の微細粒子の島相及び海相を形成する導電性の少ない高分子（ポリマーB）からなり、ポリマーB自身が有する導電性と場合によってはポリマーBに添加される主として電子導電性付与剤により、全体として十分な導電性を与えらる。

【0009】 しかし、導電性高分子組成物のもつ導電性全体において、導電性の小さい高分子（ポリマーB）の導電性の寄与が大きくなると、添加されている導電性充填剤の影響で抵抗のばらつきや経時変化が大きくなる短所があるので、イオン導電性を有する高分子（ポリマーA）の配合量が多い方が好ましい。具体的には、ポリマーA/ポリマーBの配合量（重量）の比は90/10、0~20/80の範囲がよいが、好ましくは85/15~40/60、さらに好ましくは80/20~50/50の範囲である。イオン導電性を有する高分子（ポリマーA）が90

樹脂料や有機顔料などを必要に応じて添加できる。

【0031】

以下に実施例、比較例を挙げて、本発明を更に具体的に説明する。本発明はその要旨を超えない限り、以下の実施例に限定されるものではない。

実施例1～8、比較例1～8

ポリマーA、ポリマーB及び各種配合剤を表1～4に示す配合量で配合した。配合量の単位は重量部である。

【0032】表1、表2、表3および表4における加工

方法の欄に記載したa、b、c、dは下記の方法を用いて混練り加工したことを示している。

a：混練り機の設定温度を約180℃にして、ポリマーAを含むマスターバッチAとポリマーBを含むマスターバッチBを混練りしながら、ポリマーAのみを加硫させる薬品を添加して、ポリマーAを動的に加硫させる。その後、ファイナル練りの加硫剤および加硫剤を添加して、約100℃で混練りしたものを混練り機から取り出してプレスで成形する。

【0033】b：混練り機の設定温度を約140℃にして、ポリマーAを含むマスターバッチAとポリマーBを含むマスターバッチBを混練りしながら、ポリマーAのみを加硫させる薬品を添加して、ポリマーAを動的に加硫させる。その後、ファイナル練りの加硫剤を添加して、約100℃で混練りしたものを混練り機から取り出してプレスで成形する。

【0034】c：混練り機の設定温度を約180℃にして、マスターバッチAを混練りした後一旦混練り機から取り出して冷却する。その後、混練り機内で加硫剤を添加して約100℃で混練りを行ったものを取り出して、プレスで成形する。

d：混練り機の設定温度を約180℃にして、マスターバッチA及びマスターバッチBを混練りする。その後、混練り機内で加硫剤を添加して約100℃で混練りを行ったものを取り出して、プレスで成形する。

また、表1～表4で注を付したものの詳細は以下の通りである。

【0035】

【表1】

ポンがかなりの割合で入り込み、ポリマーAが電子伝導性を有し電気抵抗のばらつきが大きくなりやむを得ず電圧変動を受け易い。またポリマーBに必要な電子導電性を付与できなくなるおそれもある。

【0028】なおポリマーAとポリマーBの相溶性が低い場合、ポリマーAがポリマーB中にうまく分散せず、導電性が不安定となる。そのためポリマーAとポリマーBの間の相溶性を高めて、ポリマーAがポリマーB中に微分散させる必要がある。ポリマーAとポリマーBの相溶性を調べるのは、通常用いられる溶解度パラメーター、すなわちSP値（単位 $\text{cal}^{1/2} \cdot \text{cc}^{-1/2}$ ）を用いるのが簡便である。ポリマーAとポリマーBのSP値の差が2以上ある場合は、相溶性に問題が出てくる可能性がある。このような場合は、ポリマーAとポリマーBの両成分を一分子中に有するよう物質、もしくはポリマーAとポリマーBの間のSP値を持つ物質を動的に加硫時に添加すると良い。このようにポリマーAとポリマーBの相溶性を改善する物質を相溶化剤と呼ぶ。SP値の差が2以上ある場合には、相溶化剤を添加することによって、相溶化剤のない場合にはポリマーAがポリマーB中に微分散しない系でも、微分散させることができ、導電性を安定かつ良好に保つことが出来る。

【0029】使用する相溶化剤はポリマーAとポリマーBの種類により変わるのは当然であるが、相溶化剤の使用量はポリマーAとポリマーBの合計100phrに対して、おおよそ30phr以下、好ましくは20phr以下である。相溶化剤は1種類、もしくは2種類以上使用することが出来る。ポリマーAとポリマーBのSP値の差が大きい場合は、相溶化剤をたとえ2種用いると、ポリマーAと相溶化剤1のSP値の差を2以内に、また相溶化剤2と相溶化剤2のSP値の差を2以内に、相溶化剤2とポリマーBのSP値の差を2以内にすることによって、全体の相溶化を円滑にすると共に、相溶化剤全体の量を減らすことができる。

【0030】これらの他にも、ポリマーAおよび/もしくはポリマーBに酸化防止剤、シリカ、クレイ、炭酸カルシウム等の充填剤、ミネラルオイル等の軟化剤、ジオクチルフタレート（DOP）、ジオクチルアジベート（DOA）等の可塑剤、酸化チタン、ベンガラ、等の無

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	実施例1	実施例2	実施例3	実施例4
マスターバッチA ポリマーA1 ¹⁾ ポリマーA2 ²⁾ イオン導電性付与剤1 ³⁾ イオン導電性付与剤2 ⁴⁾ 相溶化剤1 ⁵⁾ 相溶化剤2 ⁶⁾ 界面活性剤1 ⁷⁾ 受硫剤1 ⁸⁾ 受硫剤2 ⁹⁾	— 50 — — 7.5 — — 8.6 —	80 — — 12.0 — — — — —	80 — 4.0 — 4.0 — — — — 8.0	80 — — 5.0 12.0 — — — — 8.0
マスターバッチB ポリマーB1 ¹⁾ ポリマーB2 ²⁾ ポリマーB3 ³⁾ ポリマーB4 ⁴⁾ 相溶化剤1 ⁵⁾ 相溶化剤3 ⁶⁾ 界面活性剤1 ⁷⁾ 受硫剤1 ⁸⁾ 受硫剤2 ⁹⁾	50 — — — 7.5 — — 1.1 —	— 20 — — 3.0 — — — —	— 20 — — 2.0 — — — —	— 20 — — 3.0 — — — —
動的加硫用添加剤 加硫促進剤1 ¹⁾ 加硫促進剤2 ²⁾ 加工助剤 ³⁾ 重粉炭 ⁴⁾ 加硫剤1 ⁵⁾ 加硫剤2 ⁶⁾	0.8 0.8 1.0 — 0.8 —	— 0.4 1.0 — — 0.7	— 0.4 1.0 — — 0.7	— 0.4 1.0 — — 0.7
ファイナル練り用添加剤 導電性充填剤1 ¹⁾ 加工助剤 ²⁾ 重粉炭 ³⁾ 加硫促進剤3 ⁴⁾ 加硫促進剤4 ⁵⁾ 加硫剤3 ⁶⁾	1.1 1.0 2.5 0.5 — —	— 1.0 1.0 — 0.2 0.2	6 1.0 1.0 — 0.2 0.2	5 1.0 1.0 — 0.2 0.2
加工方法	a	a	a	a

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11	実施例5	実施例6	実施例7	実施例8
マスターバッチA ポリマーA1 ポリマーA2 イオン導電性付与剤1 イオン導電性付与剤2 相溶化剤1 相溶化剤2 界面活性剤1 受酸剤1 受酸剤2	8.0 — — — 12.0 — — — — 8.0	— 5.0 — — — 3.0 — 8.0 —	— 5.0 — — — — 1.0 7.5 —	5.0 — — — — — — — — 5.0
マスターバッチB ポリマーB1 ポリマーB2 ポリマーB3 ポリマーB4 相溶化剤1 相溶化剤3 界面活性剤1 受酸剤1 受酸剤2	— — 2.0 — — 3.0 — — — —	5.0 — — — — — 3.0 — 0.5 —	5.0 — — — — — 1.0 — —	— — — 5.0 — — — — 5.0
動的加硫用添加剤 加硫促進剤1 加硫促進剤2 加工助剤 重鉛華 加硫剤1 加硫剤2	— 0.4 1.0 — — — 0.7	0.8 0.8 1.0 — 0.8 —	0.8 0.8 1.0 — 0.8 —	0.8 0.8 1.0 2.5 0.8 —
ファイナル練り用添加剤 導電性充填剤1 加工助剤 重鉛華 加硫促進剤3 加硫促進剤4 加硫促進剤7 加硫剤3	5 1.0 — — — — —	1.1 1.0 2.5 0.5 — — —	1.1 1.0 2.5 0.5 — — —	1.1 1.0 — — — — —
加工方法	a	a	a	b

[0037]

40 [表3]

13	比較例1	比較例2	比較例3	比較例4
マスターバッチA ポリマーA1 ポリマーA2 ポリマーA3** イオン導電性付与剤1 イオン導電性付与剤2 相溶化剤1 相溶化剤2 受酸剤1 受酸剤2 導電性充填剤2***	100 — — — — — — — — 10 —	100 — — 5.0 — — — — — 10 —	— — — — — — — — — — —	— 5.0 — — — 7.5 — 8.6 — — —
マスターバッチB ポリマーB1 ポリマーB2 ポリマーB5** 相溶化剤1 受酸剤1 受酸剤2	— — — — — — —	— — — — — — —	100 — — — — — —	5.0 — — — 7.5 1.1 —
動的加硫用添加剤 加硫促進剤1 加硫促進剤2 加硫促進剤6*** 加工助剤 重鉛華 加硫剤1 加硫剤2	— — — — — — — —	— — — — — — — —	— — — — — — — —	— — — — — — — —
ファイナル練り用添加剤 導電性充填剤1 加工助剤 重鉛華 加硫促進剤3 加硫促進剤4 加硫促進剤5*** 加硫促進剤7*** 加硫剤3 加硫剤4***	— 1.0 5.0 — — 1.5 1.5 1.5 — —	— 1.0 5.0 — — 1.5 1.5 1.5 — —	23 1.0 5.0 1.0 — — — — — —	20 1.0 5.0 0.5 — — 0.8 0.8 0.8 — —
加工方法	c	c	c	d

[0038]

[表4]

実施例1	実施例2	実施例3	実施例4
○	○	○	○
ポリマーAのlog ₁₀ R _g	8.6	8.2	7.0
ポリマーBのlog ₁₀ R _g	8.9	8.5	8.5
導電性高分子組成物のlog ₁₀ R	8.7	8.3	7.3
体積固有抵抗のばらつきΔlog ₁₀ R ₁	0.3	0.2	0.2
体積固有抵抗の経時変化Δlog ₁₀ R ₂	0.2	0.2	0.3
体積固有抵抗の環境依存性Δlog ₁₀ R ₃	0.2	0.4	0.4

【表6】

- 成形した後、プレス成形機により、適正温度で最速時間プレスを行った。プレス後、表面を研磨し2mm厚にし、その後導電性高分子組成物の体積固有抵抗Rを測定し、体積固有抵抗値log₁₀Rを求めた。表5、表6、表7、表8に各実施例及び比較例の評価結果を示した。
- 【0054】尚、転写ペルトとして用いる場合は研磨後のゴム厚を0.50±0.05mmとなるように研磨した後、必要に応じてウレタン樹脂等のコート剤を塗布した後、必要に応じて塗布、焼成する。必要に応じてコート剤を塗布、焼成するのは、転写ロール等でも同様であるが、コート剤を付した場合はそのコート剤も含めた製品としての体積固有抵抗値R₀が先に述べたような10⁴～10¹²(Ω・cm)となることを要しない。
- 【0055】一般に約10μm程度のウレタン樹脂コート剤によるコート層をもうけた場合、上記のゴム厚0.50±0.05mmの転写ペルトでは、製品としての体積固有抵抗は約0.5～1乗程度上昇する。
- 【0056】1) 体積固有抵抗Rの測定方法
体積固有抵抗値R(Ω・cm)の測定は、JIS K 6911「熱硬化性プラスチック一般試験方法」記載の体積抵抗率の測定方法に準拠して行なった。得られたサンプルについて、体積固有抵抗log₁₀Rを算出した。体積固有抵抗のばらつき、経時変化および環境依存性の測定方法は以下の通りである。
- 2) 体積固有抵抗のばらつき
各実施例及び比較例で得たサンプルを各々8個用意し、各8個のサンプルの体積固有抵抗を測定し、その最大値と最小値との差Δlog₁₀R₁を求めた。この差が大きいのほど、体積固有抵抗のばらつきが大きくなる。
- 3) 体積固有抵抗の経時変化
各実施例及び比較例で得たサンプル8個ずつを用意し、室温下で4週間放置した。そして、サンプリング直後、1週間後、2週間後、3週間後、4週間後の計5回にわたって各サンプルの体積固有抵抗を測定し、各々の時点において各実施例・比較例毎の各8個の平均値を求め、この平均値の最大値と最小値との差Δlog₁₀R₂を求め、サンプル8個の平均値を求めた。この差が大きいのほど、体積固有抵抗の経時変化が大きくなる。
- 4) 体積固有抵抗の環境依存性
温度10℃、相対湿度15%の環境下及び温度32.5℃、相対湿度90%の環境下に、各実施例および比較例で得たサンプル8個ずつをそれぞれ2.4時間放置し、それぞれの環境下での体積固有抵抗の平均値を求め、得られた2つの平均値の差Δlog₁₀R₃を求めた。
- 5) プリード性の測定方法
サンプルを温度23℃で湿度55%の雰囲気下で1週間放置し、材料表面に液状のにじみが出ているかどうかを目視、触感および濾紙を用いて次の3段階に分けて評価する。
- 【0057】
×：目視でにじみだしが確認されるとき、又は手で触った感じが感じられるとき
△：目視でにじみだしが確認されず、手で触ってみてべたつきが感じられないが、サンプルに濾紙を当ててこするとイオン導電性付与剤等の液状物が濾紙へ移行しているのが確認できるとき。
- 【0058】○：目視でにじみだしが確認されず、手で触ってみてべたつきが感じられず、更にサンプルに濾紙を当ててこすると液状物が濾紙へ移行しているのが確認されないとき。
- 6) log₁₀R_A及びlog₁₀R_Bの測定方法
各実施例および比較例におけるlog₁₀R_Aまたはlog₁₀R_Bは、次のようにサンプルを作成して求めた。
【0059】マスバッチAの組成物に動的加磁用の加磁促進剤、加磁剤、加工助剤を後述の配合量で添加し、混練りして得られた組成物をプレス成形機により適正温度で最速時間プレスを行った。プレス後表面を研磨し2mm厚にした後R_Aを測定し、体積固有抵抗値log₁₀R_Aを求めた。なお、動的加磁用の加磁促進剤、加磁剤、加工助剤の配合量は、表1～4に示されているこれらの添加剤の各配合量に、各実施例または比較例における(ポリマーA+ポリマーB)/ポリマーAの重量比をかけた量を加算した。
- 【0060】マスバッチBの組成物にファイナル練り用の導電性充填剤、助剤(亜鉛華)、加磁剤、加磁促進剤を後述の配合量で添加し、混練りして得られた組成物をプレス成形機により適正温度で最速時間プレスを行った。プレス後表面を研磨し2mm厚にした後R_Bを測定し、体積固有抵抗値log₁₀R_Bを求めた。なお、ファイナル練り用の導電性充填剤、助剤(亜鉛華)、加磁剤、加磁促進剤の配合量は、表1～4に示されているこれらの添加剤の後の各配合量に、各実施例または比較例における(ポリマーA+ポリマーB)/ポリマーBの重量比をかけた量を加算した。
- 7) 水蒸気透過係数Pの測定方法
ポリマーBの水蒸気透過係数P₁(g/cm・hr)は、JIS Z 0208に準拠して求めた透過度M(g/m²・2.4hr)を(2)式により1時間、透過面積1cm²および試験片の厚み1cmあたりに換算して得られた値である。すなわち、試験片の厚みT(cm)、としたとき
【0061】
P=M/(2.4×10000×T) (2)
により算出される。
【0062】
【表5】

【0063】

	実施例5	実施例6	実施例7	実施例8
フリード性	○	○	○	○
ポリマーAの $\log_{10}R_s$	8.2	8.5	8.5	8.2
ポリマーBの $\log_{10}R_s$	8.6	8.9	8.9	8.8
導電性高分子組成物の $\log_{10}R$	8.3	8.7	8.7	8.5
体積固有抵抗のばらつき $\Delta\log_{10}R_s$	0.3	0.3	0.3	0.2
体積固有抵抗の経時変化 $\Delta\log_{10}R_s$	0.3	0.3	0.3	0.2
体積固有抵抗の環境依存性 $\Delta\log_{10}R_s$	0.4	0.1	0.2	0.3

[0064]

[表7]

	比較例1	比較例2	比較例3	比較例4
フリード性	○	△	○	○
ポリマーAの $\log_{10}R_s$	8.2	6.6	-	-
ポリマーBの $\log_{10}R_s$	-	-	8.5	-
導電性高分子組成物の $\log_{10}R$	8.2	6.6	8.5	6.4
体積固有抵抗のばらつき $\Delta\log_{10}R_s$	0.1	0.2	1.5	1.6
体積固有抵抗の経時変化 $\Delta\log_{10}R_s$	0.3	0.3	0.8	0.9
体積固有抵抗の環境依存性 $\Delta\log_{10}R_s$	1.5	1.9	0.1	0.3

[0065]

[表8]

	比較例 5	比較例 6	比較例 7	比較例 8
フリード性	○	○	○	○
ポリマーAのlogR ₁ R ₂	8.6	8.6	8.2	8.5
ポリマーBのlogR ₁ R ₂	7.5	14.0	10.0	9.2
導電性高分子組成物のlogR	7.6	13.1	9.1	8.8
体積固有抵抗のばらつきΔlogR ₁ R ₂	1.6	0.3	0.1	1.6
体積固有抵抗の経時変化ΔlogR ₁ R ₂	0.8	0.2	0.2	1.0
体積固有抵抗の環境依存性ΔlogR ₁ R ₂	0.1	1.1	1.7	0.2

[0066]

【発明の効果】 イオン導電性を有するポリマーAと導電性の少ないポリマーBを動的加電により、ポリマーAを

ポリマーB中に分散、加電させることにより、環境依存性が少なく、かつ電気抵抗の安定した、経時変化の少ない導電性高分子組成物を得ることが出来る。

フロントページの続き

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